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DETERIMINATION OF UNSATURATED HYDROCARBONS IN GASOLINE

BY

E. W. DEAN AND H. H. HILL

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DETERMINATION OF UNSATURATED HYDROCARBONS IN GASOLINE.

By E. W. Dean and H. H. Hill.

INTRODUCTION.

At present one of the most important factors in gasoline production is the so-called pressure cracking process. As the transformation of heavy petroleum products into motor fuel is one of the most desirable methods of increasing the country's supply of gasoline and preventing the threatened shortage of this necessary fuel, much attention has been given to that branch of petroleum technology, with the result that many cracking processes, employing various procedures, have been devised.

Of the various cracking processes known in September, 1917, only one had attained any considerable commercial development. This single process, however, which is owned and controlled by an oil company, is so extensively operated that it is estimated to have produced 3,000,000 barrels of gasoline out of the total 41,000,000 marketed during the calendar year 1915.[a]

Cracked petroleum products, as first made, contained noticeable percentages of olefins or unsaturated hydrocarbons. Such constituents were formerly considered undesirable in gasoline and the process of refining was so conducted that their content in market products was minimized. At present the evidence at hand shows that gasolines containing up to 12 per cent of unsaturated constituents are satisfactory motor fuel, and it is generally conceded that products containing considerably more than 12 per cent of olefins can be used without trouble. Claims for the superiority of "unsaturated" gasolines[b] have even been made, and indications have been obtained in experimental work being conducted by the bureau which also point toward advantageous qualities of cracked gasoline.

[a] Report of the Secretary of the Interior to the U. S. Senate: Senate Doc. 310, Feb. 2, 1916, p. 18.

[b] Hall, W. A., Address before Institution of Petroleum Technologists, London, Feb. 18, 1915. Abstracted in Petroleum World, vol. 12, March, 1915. pp. 137–149.

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One phase of the problem of unsaturated hydrocarbons in gasoline, which is independent of commercial considerations, demands attention. In the laboratory it is frequently desirable to determine just how "unsaturated" a gasoline is, and a satisfactory laboratory method that will furnish this information is needed. The obtaining of such information will often show the source of a gasoline and tell much about its method of production.

This report does not present any radically new data, but is concerned chiefly with the correlation of existing information. Various laboratory methods were studied and experiments made. The study has dealt chiefly with methods that are frequently used without an adequate knowledge of the theoretical and experimental principles involved. The experimental work has dealt with the development of recognized methods to an optimum of convenience in use and with the comparison of the numerical results of the various methods.

ACKNOWLEDGMENTS.

A number of determinations of iodine numbers and percentages of sulphuric-acid absorption were made by W. A. Jacobs, of the petroleum division of the Bureau of Mines.

Krämer and Böttcher bottles were provided through the kindness of David T. Day, consulting chemist of the Bureau of Mines.

CHEMISTRY OF "UNSATURATION."

A thorough discussion of the chemistry of the hydrocarbons found in petroleum and petroleum products would be too lengthy for this paper and would have no practical value, but a clear understanding of the basic principles involved is essential. For this reason the chemical properties of the various classes of petroleum hydrocarbons are briefly discussed here, but as exceptions are known to exist these statements must be understood to apply only in a general way. Only those exceptions of practical importance have been taken into account.

The commonly accepted usage in the petroleum industry is to consider as "unsaturated" only the olefin and the acetylene hydrocarbons. The term "aromatic" is reserved for hydrocarbons of the benzene series, which, although unsaturated as regards molecular structure, differ radically from olefins in chemical activity.

The general principles upon which methods for the analysis of hydrocarbon mixtures depend are evident from the following outline of properties of the different classes of compounds:

Paraffins are of relatively low specific gravity and are chemically inert.

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Naphthenes are of somewhat higher specific gravity than paraffins and are chemically inert.

Olefins, including hydrocarbons having one or more double linkages between carbon atoms, have about the same specific gravity as paraffins, but are subject to various chemical reactions; the most important of these are the addition of halogens and combination with ordinary concentrated sulphuric acid.

Acetylenes have, in addition to most of the olefin reactions, the power of combining with certain metallic salts. Acetylene hydrocarbons do not seem to occur extensively in petroleum mixtures, probably because they tend to change into aromatic hydrocarbons.

Aromatic hydrocarbons have relatively high specific gravities and occupy an intermediate position as regards chemical activity. They do not react with ordinary concentrated sulphuric acid readily, but can be made to combine with fuming sulphuric acid ("oleum"). They can be nitrated if treated under proper conditions with a mixture of nitric and sulphuric acid. Aromatic hydrocarbons can be made to combine with bromine and chlorine under properly regulated conditions, but do not take up iodine directly.

SCOPE OF INVESTIGATION.

The experiments described herein have dealt chiefly with the estimation of unsaturated constituents in mixtures that also contain paraffin or paraffin and aromatic hydrocarbons. Allowance has been made for the presence of aromatics in only the moderate proportion usual with petroleum products. The problem of estimating aromatic constituents is not considered, as none of the experiments recently performed has shown any method to be better than that described in a recent paper by Rittman, Twomey, and Egloff.[a]

The methods in common use for the estimation of "degree of unsaturation" have been studied in detail and data obtained that show the general relations existing among the results of these methods. The widely used "acid-heat test" proves little better than qualitative and that its results are decidedly unreliable for highly unsaturated gasolines. The method of absorption by sulphuric acid and the iodine absorption method were both found to have advantages, with the balance decidedly in favor of the former. The results of either of these methods can be converted into terms of the other in a roughly approximate way, but exact agreement can not be expected, owing to differences in the mechanism of the reactions involved.

Comparison of the bromine absorption method with the iodine method showed the advantage to lie with the latter.

[a] Rittman, W. F., Twomey, T. J., and Egloff, Gustav; The estimation of aromatic hydrocarbons in cracked petroleum mixtures: Met. and Chem. Eng., vol. 13, October, 1915, pp. 682–686.

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The work of the present investigation may be summarized as indicated in the following outline:

1. Study of experimental methods:
   (*a*) Hanus iodine method as applied to cracked gasoline.
   (*b*) Modifications of the method of absorption by sulphuric acid.
   (*c*) Modifications of the Maumené test or "acid-heat test."
   (*d*) Bromine absorption method.
2. Comparison of the results of the several methods.

EXPERIMENTS.

DETERMINATION OF IODINE NUMBERS BY THE HANUS METHOD.

The Hanus[a] method of determining iodine numbers seems to be the most advantageous of any yet devised for this purpose. It is more rapid than the widely used Hübl[b] method and does not require the special reagents employed in the Wijs[c] method.

The factors of time and concentration are adequately discussed by Smith and Tuttle,[d] who recommend that a 30-minute absorption period be employed and that the quantities of Hanus solution and unknown oil be so adjusted that at the end of the reaction there remains an excess of unabsorbed iodine equivalent to 70 to 90 per cent of the quantity originally used. However, the specific recommendation regarding concentration of reagents made by these investigators for testing petroleum oils should be disregarded in favor of the more general recommendation, as their work concerned only petroleum products having a low degree of unsaturation.

PROCEDURE USED IN EXPERIMENTS.

PREPARATION OF SOLUTIONS.

The Hanus iodine solution is made by dissolving 13.2 grams of iodine and 3 c. c. of bromine in a liter of glacial acetic acid. This solution should be allowed to stand several days before using.

Sodium thiosulphate solution is prepared by dissolving approximately 25 grams of the crystallized salt ($Na_2S_2O_3.5H_2O$) in each liter of water.

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[a] Hanus, J., Die Anwendung von Jodmonobromid bei der Analyse von Fetten und Oelen: Ztschr. Unters. Nahr. Genuss., vol. 16, 1901, pp. 913–920. Hunt, F. W., A comparison of methods used to determine the iodine values of oils: Jour. Soc. Chem. Ind., vol. 21, 1902, pp. 454–455. Smith, W. H., and Tuttle, J. B., Iodine numbers of linseed and petroleum oils: Bureau of Standards Tech. Paper 37, 1914, pp. 1–14.

[b] Hübl, —, Eine allgemein anwendbare Methode zur Untersuchung der Fette; Dingler's Poly. Jour., Bd. 253, 1884, pp. 281–295; Jour. Soc. Chem. Ind., vol. 3, 1884, pp. 641–643.

[c] Wijs, J. J. A., Zur Jod-Additionsmethode: Ber. Deut. Chem. Gesell., vol. 31, 1898, pp. 750–752.

[d] Smith, W. H., and Tuttle, J. B., place cited.

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Potassium dichromate solution is prepared by dissolving 3.8663 grams of very pure dry salt ($K_2Cr_2O_7$) in water and making up the volume to a liter. This is the basic standard solution for this method and must be prepared and preserved with great care. The quantity taken will liberate 10 grams of iodine from an acidified solution of potassium iodide.

Potassium iodide solution is made by dissolving one part by weight of the pure salt in nine parts of water.

Starch indicator solution may be prepared in various ways. The method of Gooch[a] is highly satisfactory; 5 grams of starch is mixed with a tiny bit (about 0.01 gram) of red mercuric iodide and rubbed to a smooth paste with cold water. This paste is poured into a liter of vigorously boiling water and stirred thoroughly, the boiling being continued for a minute or two. The solution is allowed to cool and settle; the clear portion is decanted into a bottle from which it is used. About 3 c. c. is used in each titration. If red mercuric iodide is not available the solution may be prepared without it, and when cold shaken with a few drops of chloroform, which acts as a preservative.

STANDARDIZATION OF SOLUTIONS.

Sodium thiosulphate solution is standardized against the potassium dichromate solution as follows: 25 c. c. of the latter, equivalent to 0.25 gram of iodine, is run from a pipette into a 200-c. c. Erlenmeyer flask containing about 12 c. c. of a 10 per cent solution of potassium iodide and 5 c. c. of ordinary concentrated, chemically pure, hydrochloric acid. The iodine thus liberated is titrated with sodium thiosulphate solution, the standard of the latter being recorded in grams of iodine equivalent to each cubic centimeter of the thiosulphate solution. The thiosulphate solution needs to be restandardized occasionally, as it changes slightly on standing.

The Hanus iodine solution is standardized daily in the regular course of making determinations by "running a blank"—that is, titrating a mixture made up like one of the unknown mixtures but without any gasoline.

METHOD OF DETERMINATION.

The general scheme of procedure is as follows: Reaction mixtures are made up in the special glass-stoppered Erlenmeyer flasks sold for the purpose by chemical supply houses. The mixtures may be prepared at uniform intervals (5 minutes is a convenient period) until 30 minutes have elapsed, when the first mixture is titrated. One of the factors that insures agreement of results is uniform time of re-

[a] Gooch, F. A., Methods in chemical analysis. New York, 1912, 536 pp.

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action, and the 30-minute period recommended by Smith and Tuttle[a] should not be allowed to vary more than two or three minutes either way. Determinations may be run conveniently in series of six, as each mixture can be made up in a 5-minute period and the titration can be performed conveniently in that interval of time.

The procedure for a single sample is as follows: First, 10 c. c. of chloroform or carbon tetrachloride is measured into one of the glass-stoppered reaction flasks. The proper quantity of gasoline is then measured in, care being taken that there is no loss through evaporation. A convenient method of accomplishing this involves the use of a small capillary pipette made from glass tubing of about 1 mm. internal diameter and marked at intervals along its length. The volume from the pointed tip to each of the marks is determined by weighing the pipette first empty, and then filled with pure distilled water, measured at a temperature of 15° C. Different known quantities of gasoline, measured at the same temperature, can therefore be delivered from this instrument. The density of the gasoline should be known, measured for 15/15° C. The quantity used should be such that 10 to 30 per cent of the iodine used is absorbed. It is not always possible to hit on the right ratio between Hanus solution and gasoline at the first trial, but a second determination should always bring the quantities within the proper limits.

The capillary pipette, after being filled with the gasoline (at a temperature of 15° C.), is discharged with its tip held below the surface of the chloroform or carbon tetrachloride in the flask. The empty pipette is then partly washed by filling it once with the diluted gasoline mixture and letting the contents drain out. Washing is completed by filling once with pure solvent (chloroform or carbon tetrachloride) and draining again into the flask. This procedure avoids exposure of a large surface of pure gasoline to the air and reduces evaporation losses to a negligible quantity. In the present work the quantity of Hanus solution used was 10 c. c., and the quantities of gasoline between 0.04 and 0.20 gram.

The reaction mixture is allowed to stand for 30 minutes, preferably in the dark and never in direct sunlight. At the end of this time 25 c. c. of potassium iodide solution is poured in and 100 c. c. of distilled water added. The mixture is then titrated with the standardized sodium thiosulphate solution, care being taken to shake the mixture vigorously as soon as the yellow color fades in the aqueous layer. This precaution is to insure the removal of the iodine dissolved in the carbon tetrachloride or chloroform layer at the bottom of the flask. The starch indicator should not be added until after

[a] Smith, W. H., and Tuttle, J. B., Iodine numbers of linseed and petroleum oils: Bureau of Standards Tech. Paper 37, 1914, pp. 1–14.

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the yellow color of the iodine becomes faint. Warning of the approaching end of the titration is given by the color changing from greenish to blue. The titration is complete when the blue color just fades.

The iodine number is the percentage by weight of iodine absorbed and is calculated by the following procedure: The titer of the unknown mixture is subtracted from that of a blank, consisting of Hanus solution and solvent allowed to stand 30 minutes without any gasoline, and the difference in cubic centimeters of thiosulphate solution is multiplied by the weight of iodine equivalent to each cubic centimeter of the solution. The weight of iodine thus found is divided by the weight of gasoline taken, and the quotient is multiplied by 100, which gives the iodine number.

RESULTS OF EXPERIMENTS.

No particular study of the details of operation of the iodine method was necessary, as the conclusions of Smith and Tuttle[a] served to indicate advantageous conditions of time and concentration. The device of using a capillary pipette for measuring the gasoline was all that was needed to make the Hanus iodine method practicable for use with volatile liquids. Figures for determinations of iodine numbers are given in pages 19 and 20, in connection with results of other methods of determining degrees of unsaturation.

METHOD OF ABSORPTION BY SULPHURIC ACID.

The method of absorption by sulphuric acid is similar in principle to the iodine absorption method, except that it involves measurement of a decrease in the quantity of the reagent. The method is more or less widely used, but generally without a knowledge of certain devices or methods of procedure that obviate experimental difficulties. When sulphuric acid is mixed with a highly unsaturated oil or gasoline there is a possibility that much heat may be developed and that gaseous reaction products may form with almost explosive violence. Some types of apparatus that are frequently used are not of proper design to minimize these difficulties and have the additional disadvantage of relatively high cost and fragility.

DISCUSSION OF VARIOUS PROCEDURES USED IN ANALYTICAL LABORATORIES.

Two of the commonly used types of apparatus and procedure deserve discussion.

[a] Smith, W. H., and Tuttle, J. B., work cited.

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SHAKING IN CYLINDRICAL GRADUATE.

A long slender graduated cylinder with a glass stopper is often used for determining the "degree of unsaturation," the procedure being to mix equal volumes of gasoline and acid, shake the mixture, and allow it to separate by standing. The difficulties involved are considerable, as these graduates are inconvenient to handle and are inefficient in that it is difficult or even impossible to mix properly light gasoline and heavy acid in this type of container. If the reaction is violent, the contents of the tube may be completely expelled.

USE OF KRÄMER AND BÖTTCHER BOTTLE.

A method that has been extensively employed in one of the petroleum laboratories of the Bureau of Mines involves the use of a slender graduated tube with a flat-bottomed bulb at the bottom. This type of apparatus is described by Holde[a] in connection with the Krämer and Böttcher method for determining aromatic hydrocarbons by the sulphonation method. It is hereafter designated as the Krämer and Böttcher bottle. Equal volumes of oil and acid are measured into the bulb and are shaken thoroughly, after which enough acid is added to bring the level of the mixture nearly to the top of the graduated part of the neck. This method is accurate and fairly satisfactory if properly conducted, but the graduated tubes are expensive, fragile, and inconvenient to handle. The single important advantage is the possibility of properly mixing oil and acid, thereby eliminating the danger of excessive heating, blowing out of the contents, and inaccurate results from incomplete absorption of the unsaturated compounds.

USE OF BABCOCK BOTTLE AND CENTRIFUGE.

An obviously advantageous modification of this method is the substitution of some one of the types of Babcock milk bottles for the inconvenient special graduate. Babcock bottles, on account of their extensive use, are cheap and easy to obtain, and are also of convenient size to handle. They will stand upright without support and can be placed in a centrifuge when a rapid separation of the acid and the gasoline layers is desired; their one disadvantage is that they can not be read as accurately as the Krämer and Böttcher bottles. This disadvantage is slight, however, as the degree of accuracy is sufficient for the purpose.

The use of Babcock bottles and a centrifuge for the determination of unsaturated hydrocarbons is described in an article by Egloff and

[a] Holde, D., The examination of hydrocarbon oils and of saponifiable fats and waxes; translated by E. Mueller. New York, 1915, p. 49.

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Twomey.[a] Their procedure was essentially modified in the authors' experiments in one important detail, the method of mixing acid and gasoline. Egloff and Twomey recommend adding acid in small quantities to the gasoline, shaking, and cooling thoroughly after each addition. In the experiments described herein a considerable excess of acid was added rapidly to the gasoline. This procedure prevents inconvenient heating of the mixture and practically eliminates the troublesome factor of gas formation.

It is, of course, natural to expect that if the addition of a little acid to gasoline produces heat and gas, the addition of more acid will produce more heat and gas. The preceding statements to the effect that keeping the acid in excess avoids such difficulties may seem paradoxical, and the following suggestions are therefore offered in explanation of these statements. In the first place the large heat capacity of the excess acid cuts down the temperature rise. In the second place it seems reasonable to suppose that the reaction should be considered as one in which the unsaturated hydrocarbons attack the acid rather than one in which the acid attacks the hydrocarbons. If the hydrocarbon concentration is low then the reaction is not violent and all that occurs is a combination, probably with the formation of sulphuric acid esters. If the hydrocarbons are in excess the reaction proceeds further and the acid is reduced with the formation of gaseous products such as sulphur dioxide.

IMPROVED METHOD.

The procedure evolved in the course of the experiments described herein is simple and has yielded satisfactory results with mixtures containing as much as 40 per cent of unsaturated hydrocarbons. The container employed is that described in the catalogues of chemical supply houses as the 6-inch, 9-gram, 40 per cent Babcock cream bottle. The neck of such a bottle is calibrated for the volume of 4.5 grams of butter fat, which is a little less than 5 c. c. An ordinary 5 c. c. pipette can be regraduated to deliver this quantity.

The gasoline to be tested is run into a clean, dry bottle, cooled for a minute or two by immersing in ice water, and then 200 per cent by volume of ordinary concentrated sulphuric acid is poured in from a small graduate. Care should be taken that the acid runs quietly down the side of the bottle, instead of splashing onto the surface of the gasoline. A rubber stopper is then placed in the bottle and the contents are shaken, first slowly, then vigorously with a rotary motion for several minutes. The gasoline and the acid are separated by either one of the following two methods.

[a] Egloff, Gustav, and Twomey, T. J., The effect of temperature on the formation of olefins at atmospheric pressure: Met. and Chem. Eng., vol. 14, Mar., 1916, pp. 247–250.

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GRAVITY SEPARATION.

Sulphuric acid is added to the contents of the bottle until the surface of the liquid is about level with the upper graduation mark on the neck of the bottle. The mixture is then set aside and allowed to stand overnight, when practically complete separation is effected.

CENTRIFUGAL SEPARATION.

The stoppered bottle is placed in a suitable centrifuge and revolved for two or three minutes at a speed of 500 to 1,000 r. p. m. Sufficient acid is then added to bring the level up to the lower graduation mark and the contents are again centrifuged to complete the separation. More acid is then added to bring the column to the upper graduation mark, after which the residual volume of gasoline is read.

ADVANTAGES OF METHOD.

The results obtained have a possible error of 1 to 2 per cent, but within these limits seem to be thoroughly reliable. After extensive comparison, the writers prefer this method to the iodine absorption method. The iodine method, if properly applied, is undoubtedly the more accurate, and, unless a centrifuge is available, may be considered more rapid. However, it requires the operator to have considerable skill in the technique of iodimentry and yields results that may involve large errors if operative details are wrong.

The sulphuric-acid method, on the other hand, is simple, reliable, although not highly accurate, and is more rapid than the iodimetric method if a centrifuge is available. If speed is measured in terms of the time required for the actual work of making up reaction mixtures, this method is more rapid even if overnight standing is employed, although a longer wait is then necessary before the results are available.

COMPARISON WITH OTHER METHODS.

The experiment with the sulphuric acid absorption method may be outlined under three heads, as follows:

1. Development of a convenient and rapid method of procedure and the adoption of satisfactory apparatus; study of the effect of mechanical details and comparison of various types of apparatus.

2. Comparison of results obtained with strengths of acid varying from about 88 per cent to about 95 per cent.

3. Study of possibility of interference from presence of aromatic hydrocarbons.

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EFFECTS OF APPARATUS AND PROCEDURE.

The use of Babcock bottles and the adoption of the method of keeping acid in excess during the reaction resulted from general considerations and a knowledge of the disadvantages of other types of procedure. It was, however, considered desirable to obtain experimental evidence on the agreement of results obtained by the two methods of separation—centrifugal and gravity. In addition, the results obtained with Babcock bottles and the Krämer and Böttcher bottle were compared.

The table following shows results of two series of tests, both involving the treatment of the gasoline with 200 per cent by volume of acid in Babcock bottles. In one series the acid and gasoline were separated by centrifuging three or four minutes, filling the bottle to the lower graduation mark, and again centrifuging for several minutes to complete the separation of the two layers. In the other series the mixture was allowed to stand overnight with the bottle filled to the upper graduation mark.

Comparison of results obtained by centrifugal and gravity separation in Babcock bottles.

No. of test.	Percentage absorbed by—	
	Centrifugal separation.	Gravity separation.
1.....	39	37
2.....	21	19
3.....	19	17
4.....	18	14
5.....	14	13
6.....	11	11
7.....	8	9

It is to be noted that all the differences fall within the admitted limits of error of the methods, but that there is a general tendency for results by the gravity method to be low.

The agreement between results with the Babcock centrifugal method and the method involving the use of the long-necked Krämer and Böttcher bottle is shown in the table following. The percentages of unsaturation indicated were practically identical.

Comparison of results with the Babcock bottle, using centrifugal separation, and with the Krämer and Böttcher bottle.

	First test.	Second test.
Absorption in Babcock bottle, per cent	39	17
Absorption in Krämer and Böttcher bottle, per cent	40	17

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EFFECTS OF VARIATIONS IN STRENGTH OF ACID USED.

Some experiments were also made to show the effect of slight variations in the strength of the sulphuric acid used. Ordinary concentrated sulphuric acid is not always uniform, as it has a strong tendency to become diluted through absorption of moisture from the air. The table following shows results obtained when the same sample of gasoline was treated with acid mixtures of different strengths between the approximate limits of 88 per cent and 95 per cent. Two methods were employed, the Babcock centrifugal and the Krämer and Böttcher bottle method. With the former method 200 per cent by volume of acid was used, with the latter 100 per cent.

Results of experiments showing slight effect of changing strength of sulphuric acid used between limits of 88 and 95 per cent.

[One sample of gasoline was treated with various strengths of acid by two different methods.]

Acid.		Percentage absorbed in Babcock bottle (centrifugal separation).		Percentage absorbed in Krämer and Böttcher bottle (gravity separation).	
Specific gravity (15°/15°C.).	Approximate acidity (percentage of H_2SO_4).	A.[a]	B.[a]	A.[a]	B.[a]
1.810	88	17	17	14.8	.....
1.820	90	17	16	15.6	.....
1.830	92	17	18	16.4	.....
1.835	93	17	.....	16.0	.....
1.837	94	17	.....	16.4	17.2
1.840	95	17	17	17.2	17.2

[a] Duplicate determinations.

From the figures in the above table it appears that slight variations in the strength of the acid make no difference if 200 per cent of acid is used and do not cause considerable variations in the percentages absorbed when only 100 per cent is used.

EFFECTS OF SULPHURIC ACID ON AROMATIC HYDROCARBONS.

Some experiments were performed to ascertain the effect of treating benzene, toluene, and xylene with sulphuric acid under the same conditions as the gasoline, for the purpose of ascertaining the degree to which these hydrocarbons react with ordinary concentrated sulphuric acid. The results, presented in the table following, show that benzene and toluene were practically unattacked by the acid but that about 10 per cent of the xylol [a] was absorbed. In actual fact, the

[a] "Xylol" is used as a convenient term for the usual mixture of isomeric xylenes.

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total percentage that would have been absorbed if the treatment had been continued would undoubtedly have been even greater. The results show, however, that brief treatment removes only a fraction of the xylol, and as this constituent is rarely present in more than moderate proportions it is unlikely that the error introduced through its presence could exceed 1 or 2 per cent.

Results of experiments showing slight effect of ordinary sulphuric acid on aromatic hydrocarbons.

Mixture used.	Per cent absorbed by Babcock bottle method.		Per cent absorbed by Krämer and Böttcher method.	
	A.	B.	A.	B.
25 per cent benzene and 75 per cent uncracked gasoline	1.0	1.9	.....	.....
10 per cent toluene and 90 per cent gasoline	1.0	1.0	0.4	0.4
100 per cent xylol	10.0	.....	.....	.....

MAUMENÉ TEST OR "ACID HEAT TEST."

A method largely used in the laboratories of refineries for determining the degree of unsaturation is the "acid heat test," which is practically identical with the Maumené[a] test, sometimes used in the testing of turpentine and fatty oils. This method really involves measuring the heat of reaction of oil and acid, conditions being regulated so that the heat of reaction is proportional to the rise in temperature.

The method is commonly applied as follows: 50 c. c. of gasoline is placed in a glass-stoppered bottle, 10 c. c. of ordinary concentrated sulphuric acid added, and the mixture shaken. The temperature is taken before the acid is added and then at intervals while the mixture is being shaken. As soon as a maximum temperature is reached the reaction is considered complete and the rise in temperature, generally expressed in Fahrenheit degrees, is called the "acid heat test" of the gasoline. "Straight" refinery gasoline generally has an acid heat test of less than 10° F. and the cracked products commonly marketed usually have tests not exceeding 30° or 40° F.

METHOD IS NOT SUITABLE FOR GASOLINE.

Several details of the procedure mentioned are open to criticism, particularly as regards possible variations in the heat capacities of the containers used and the heat losses through radiation. Several

[a] Maumené, M., De l'analyse des huiles au moyen de lácide sulfurique: Compt. rend., t. 35, 1852, pp. 572–573. Leach, A. E., Food inspection and analysis, New York, 1914, 3d edition, p. 494.

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other variables that might introduce errors would have been studied in the present investigation if a fundamental difficulty had not been discovered that makes the method essentially inaccurate for gasoline. The difficulty is simply that gasoline is such a volatile substance that part of the heat developed is dissipated in causing vaporization, instead of producing a rise in temperature. The error thus introduced is not considerable when the acid heat test is low, but with even moderately highly unsaturated gasoline is so large as to make the results entirely unreliable.

EXPERIMENTS TOWARD MINIMIZING MECHANICAL SOURCES OF ERROR.

Before any experimental evidence was obtained regarding the importance of this discrepancy some experiments were performed with a view toward minimizing or obviating mechanical sources of error. It was thought in particular that the differences due to variable heat capacities of containers and losses of heat through radiation could be eliminated by using a vacuum bottle instead of an ordinary thick-walled reagent bottle. This principle was utilized by Tortelli,[a] who used a vacuum vessel and a mechanical stirrer in testing animal and vegetable oils by the Maumené reaction.

USE OF VACUUM BOTTLE AND MECHANICAL STIRRING COMPARED WITH USE OF ORDINARY BOTTLE AND SHAKING.

Vacuum bottles are now in such common use that they are readily obtainable and can be purchased at moderate prices. The usual metal or leather container is neither essential nor desirable, the so-called filler being all that is required. The bottles used in the experiments by the writers were of pint size and cost about a dollar apiece. A reaction vessel of this type practically eliminates losses of heat by radiation, and, owing to the thinness of the glass, is of such small heat capacity that the possibility of variation through variable heat capacity is largely reduced.

Also it was thought that more uniform results could be obtained if the acid and the gasoline were mixed with a mechanical stirrer and not by shaking. Results showing the relative merits of the shaking and the stirring methods with the vacuum bottle and of the ordinary shaking method with a plain glass bottle appear in the table following. The reader should note that no errors or discrepancies can increase the rise in temperature except possibly excessive

[a] Tortelli, M., Thermoleometer, Ein Apparat der gestattet Verfalschungen von Oliveöl und auch andere Pflänzen- und Tierölen zu erkennen: Chem. Centralb., Jahrg. 75, 1904, 1424–1426.

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stirring, and it is, therefore, obvious that the method giving the highest results is the most accurate.

Results of "acid heat test" by three different methods.

[50 c. c. of gasoline and 20 c. c.[a] of acid were used in each test.]

Sample No.	Vacuum bottle.		Shaking in ordinary bottle.
	Stirring.	Shaking.	
	°C.	°C.	°C.
1.....	89	83	63
2.....	60	61	48
3.....	41	53	39
4.....	34	38	36
5.....	16	30	24
6.....	15	26	14
7.....	12	11	7

[a] Twenty c. c. of acid was found to be a better quantity than 10 c. c. for gasolines of a high degree of unsaturation.

The figures in the above table show that the results obtained with the vacuum bottle are always higher than those obtained with an ordinary glass bottle and that the theoretical indications of the superiority of the former are substantiated. The fortunate and convenient fact that shaking yields higher results than mechanical stirring is also shown. Each of the figures in the table represents the average of several determinations, individual figures varying over a range of 3° or 4° C.

CONCLUSIONS FROM RESULTS OF EXPERIMENTS.

To determine optimum conditions for the acid heat test, possibly a number of other variables should be studied, such as relative quantities of acid and gasoline, the strength of the acid used, and the rate of adding acid to gasoline. In the experiments described herein these factors were fixed arbitrarily, thereby eliminating possible variations from such causes, but no attempt to discover the most favorable conditions was made. The study of the acid heat test, as previously stated, was not continued because of the early discovery of the uncontrollable factor of heat losses through vaporization of the gasoline.

Conclusions with regard to the merits of the acid heat test are briefly as follows: The test is of value only for gasolines of moderately low degree of unsaturation, and when operating conditions are so maintained that the rise in temperature is proportional to the heat of reaction. The container employed should always be of a standard heat capacity and fixed quantities of acid and gasoline should be used. The strength of the acid should be always the same and the rate at which it is added to the gasoline probably should be

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fixed. The rate of adding acid is a particularly important source of possible variation, because the course of the reaction is probably affected by the relative concentrations of unsaturated hydrocarbons and acid. The quantity of acid used should be sufficient to react with all the unsaturated hydrocarbons, but should not be unnecessarily large, as the excess acid absorbs heat and thus cuts down the temperature rise. The use of a vacuum bottle of about one pint capacity is decidedly advantageous in that heat losses through radiation are eliminated and its heat capacity, being small, is not liable to cause important variations. Simple shaking with a rotary motion is better than the use of a mechanical stirrer.

The experiments indicate that the acid heat test is less satisfactory in operation than the method of absorption by sulphuric acid and that the results are less reliable.

BROMINE ABSORPTION METHOD.

To supplement the study of iodine absorption, it was deemed advisable to try one of the methods involving the absorption of bromine.

DESCRIPTION OF EXPERIMENTS AND RESULTS.

The method of McIlhiney[a] seemed most promising and was selected as representative. This method involves absorption of bromine in a medium of carbon tetrachloride during a reaction period of 30 minutes. The excess of bromine is determined by adding potassium iodide solution and titrating the liberated iodine with standardized sodium thiosulphate solution. The proportion of bromine that goes to form substitution products instead of being directly added to the hydrocarbon molecules should also be determined. This is accomplished by a supplementary titration, with thiosulphate, of the iodine liberated when a neutral solution of potassium iodate is added to the reaction mixture. The true bromine addition value is found by subtracting twice the amount found by the last titration from the total quantity of bromine absorbed. The reactions involved are as follows:

1. Bromine addition (typical)—

$$\underset{\text{Ethylene.}}{C_2H_4} + \underset{\text{Bromine.}}{Br_2} = \underset{\text{Ethylene bromide.}}{C_2H_4Br_2}$$

2. Bromine substitution (typical)—

$$\underset{\text{Ethane.}}{C_2H_6} + \underset{\text{Bromine.}}{Br_2} = \underset{\text{Ethyl bromide.}}{C_2H_5Br} + \underset{\text{Hydrobromic acid.}}{HBr}$$

[a] McIlhiney, P. G., The determination of bromine absorption of oils: Jour. Am Chem. Soc., vol. 21, 1899, pp. 1084–1089.

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3. Determination of bromine substitution, which is equivalent to hydrobromic acid formation; the bromine addition value is the total bromine loss minus the sum of the equal quantities of bromine substituted and converted into hydrobromic acid—

$$\underset{\text{Hydrobromic acid.}}{6HBr} + \underset{\text{Potassium iodate.}}{KIO_3} + \underset{\text{Potassium iodide.}}{5KI} = \underset{\text{Iodine.}}{3I_2} + \underset{\text{Potassium bromide.}}{6KBr} + \underset{\text{Water.}}{3H_2O}$$

COMPARISON WITH IODINE METHOD.

Bromine numbers were determined by this method for a series of samples of varying degrees of unsaturation. With these samples the amount of bromine substituted proved to be practically a negligible quantity. Results of the tests are shown in the following table. The iodine numbers, and the theoretical bromine values, calculated from the iodine numbers by mutiplying by the ratio of the chemical equivalents of the two halogens, are also shown.

Experimentally determined bromine numbers of a series of unsaturated naphthas compared with bromine numbers calculated from iodine numbers determined by the Hanus method.

Sample No.	Bromine value, determined by experiment.	Bromine value, calculated from iodine value.	Iodine number.
1.....	162.9	165.6	263.0
2.....	103.5	91.3	144.8
3.....	78.4	80.3	127.4
4.....	72.8	72.2	114.6
5.....	60.3	55.0	87.4
6.....	49.7	41.8	66.4
7.....	35.6	29.4	46.7

CONCLUSIONS AS TO BROMINE METHOD.

The agreement between the determined and the calculated bromine numbers was reasonably good, but there was more difficulty in obtaining concordant duplicate results with the bromine than with the iodine method. Also more time was consumed in making the determinations by the bromine method and there seemed to be no advantages from its use. Greater rapidity has been claimed by some operators for the bromine method, but undoubtedly on the basis of comparison with one of the slower iodine methods, as for instance, the Hübl.

RELATIONS BETWEEN RESULTS OBTAINED BY THE SEVERAL METHODS OF MEASURING DEGREE OF UNSATURATION.

In addition to making a study of the actual methods of determining degrees of unsaturation it was thought desirable to obtain figures showing the relations between results of the several methods.

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RELATION OF "ACID HEAT TEST" VALUE TO IODINE NUMBER AND TO PERCENTAGE OF ABSORPTION IN SULPHURIC ACID.

The table following shows the results of "acid heat tests" of a series of samples, as compared with the iodine numbers and the percentages of absorption in sulphuric acid of these samples:

Results showing relation of "acid heat test" values (in degrees centigrade) with iodine numbers and with percentages of absorption by sulphuric acid.

Sample No.	Percentage of absorption by acid.	Per cent acid absorption÷Acid heat test.	Acid heat test (°C).	Iodine number÷Acid heat test.	Iodine number.
1.....	39	0.47	83	3.2	263
2.....	21	.34	61	2.4	145
3.....	19	.36	53	2.4	127
4.....	18	.47	38	3.0	115
5.....	14	.47	30	2.9	87
6.....	11	.42	26	2.5	66
7.....	8	(.73)	11	(4.2)	47

From the above figures it appears that the relations between the several values vary within rather wide limits. Moreover, the small number of results available for comparison does not permit the inference that even these extremes represent the actual limits. The possibility of variations through changes in details of operation of the acid heat test render undesirable the giving of the impression that any definite relation exists between results of this test and those of the other two methods.

For purposes of rough comparison and in the absence of more comprehensive data, it may be said that the percentage of absorption in acid is between 0.3 and 0.5 times the acid heat test value expressed in degrees centigrade, in tests made by mixing 50 c. c. of gasoline and 20 c. c. of sulphuric acid in a vacuum bottle of about 1 pint capacity. The iodine number is 2 to 3.5 times the acid heat test value in tests performed in the same way. If the acid heat test value is given in degrees Fahrenheit the factor for conversion into the percentage of unsaturation is between the limits of 0.16 and 0.28, and for transformation into the iodine number is between 1.1 and 1.9.

In this connection, the authors again emphasize the fact that the acid heat test, as usually determined for gasoline, is so thoroughly empirical that the figures given in the relations stated above must be considered as having only a roughly general accuracy.

RELATION OF IODINE NUMBER AND PERCENTAGE OF ABSORPTION BY SULPHURIC ACID.

The relation between results of the sulphuric acid and the iodine absorption methods is more important in the present connection because a considerable number of figures are available for comparison; also the two methods are accurate enough so that no considerable variations are due to experimental error.

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The values given in the previous table for percentage of acid absorption, iodine number, and ratio of the iodine number to the acid absorption of the seven samples tested are repeated in the table following, which also gives the results of a series of unsaturation measurements made by both of the two methods. These latter figures were obtained in connection with a study of the production of gasoline by the vapor-phase cracking process, the results of which will appear in a future report. The ratios found by dividing the iodine numbers by the percentages of unsaturation vary in general between the limits of 6 and 7, with occasional extremes as low as 5.3 and as high as 7.5. The average is 6.5.

Comparison of results obtained by measuring unsaturation of gasoline by the sulphuric acid absorption and the iodine absorption method.

Test No.	Percentage of acid absorption.	Iodine number.	Iodine number÷acid absorption.	Test No.	Percentage of acid absorption.	Iodine number.	Iodine number÷acid absorption.
1.....	39	263	6.7	23.....	39	249	6.4
2.....	21	145	6.8	24.....	32	249	7.2
3.....	19	127	6.7	25.....	31	213	6.9
4.....	18	115	6.4	26.....	26	157	6.0
5.....	14	87	6.2	27.....	26	164	6.3
6.....	11	66	6.0	28.....	29	161	5.5
7.....	8	47	5.8	29.....	26	142	5.4
8.....	46	293	6.3	30.....	23	155	6.8
9.....	38	270	7.1	31.....	25	146	5.8
10.....	41	257	6.3	32.....	23	161	7.0
11.....	32	208	6.5	33.....	22	149	6.7
12.....	34	215	6.3	34.....	16	114	7.1
13.....	33	214	6.5	35.....	20	114	5.7
14.....	32	229	7.1	36.....	18	95	5.3
15.....	31	204	6.6	37.....	17	112	6.6
16.....	31	231	7.5	38.....	14	84	6.0
17.....	30	190	6.3	39.....	13	97	7.5
18.....	31	214	6.9	40.....	16	109	6.8
19.....	31	212	6.8	41.....	20	120	6.0
20.....	37	245	6.6	42.....	16	112	7.0
21.....	39	254	6.5	43.....	20	114	5.7
22.....	37	248	6.7	Average ratio.....			6.5

Probably the failure to attain closer constancy in the various determinations of the ratio is not wholly due to experimental error, for there are fundamental differences in the chemical mechanism of the two reactions. Absorption by sulphuric acid is a measure of the number of hydrocarbon molecules having one or more unsaturated linkages. Iodine absorption measures the actual number of such linkages, whether single or several, in each molecule.

APPROXIMATE RATIO FOR CONVERTING IODINE NUMBER TO PERCENTAGE OF UNSATURATION.

From the evidence at hand it appears that for gasoline the ratio 6.5 can safely be used for approximate conversion of percentages of unsaturation into iodine numbers. For some cracked distillate oils, studied in another connection, the ratio was slightly lower, and for cracked residuum oils was considerably lower, indicating that more material was attacked by acid than by iodine. This variation is to

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be expected, for asphaltic material is removed by acid in common refining practice. It therefore appears that the use of the ratio of 6.5 generally should be limited to tests of gasoline and should never be employed for oils containing appreciable quantities of pitchy material.

RATIO FOR CONVERTING BROMINE AND IODINE NUMBERS.

Bromine numbers can be approximately converted into iodine numbers by multiplying the bromine number by the ratio of the chemical equivalents of the two halogens, which is $\frac{126.9}{79.9}$, or 1.59.

SUMMARY.

A study of the analytical methods for estimating unsaturated hydrocarbons, characteristic products of the cracking reaction, in gasoline gave these results:

The Hanus iodine method, if properly applied, is satisfactory for estimating the degree of unsaturation of gasoline. Determinations can be made with moderate rapidity and the results are accurate. The method, however, requires much care and some skill in the technique of iodimetry.

The sulphuric acid absorption method is rapid, reliable, and of fair accuracy. Its value depends on the use of convenient apparatus and the observance of simple but necessary precautions in the details of manipulation. This method, as employed in the experiments described in this report, is highly recommended as satisfactory for general use.

The "acid heat test" (determination of Maumené numbers) proved unreliable, especially for highly unsaturated mixtures. Primary objections are the many empirical factors involved and the dissipation of much of the heat in volatilizing gasoline instead of producing a rise in temperature. Experiments showed that the acid heat test could be made most accurately by using as a container a vacuum bottle of about 1-pint capacity, and mixing the oil and acid by hand shaking.

The bromine absorption method proved less desirable than the iodine method, although giving approximately equivalent results.

By comparing the three methods—iodine absorption, sulphuric acid absorption, and "acid heat test"—ratios were found for transforming each set of values into terms of the other. These ratios as applied to the "acid heat test" are only rough approximations. The ratio for transforming iodine numbers into terms of percentage of sulphuric acid absorption is not essentially a constant, but for cracked gasolines varies between fairly close limits. The average figure is 6.5, and most of the values fall within the limits of 6 and 7.

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